

Reply

[seal: PCT, Received 10 June 2004]

To: Chikako Aoki, Patent Office Examiner

1. International Application: PCT/JP03/02640

2. Applicant

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4. Date of Notice April 13th, 2004

5. Content of the Reply

1) Reply to opinion in regard to Reference 1

(1) Based on the electrolysis conditions of Comparative Example 1 shown in Table 1 of Reference 1, the Examiner pointed out as reasons for Claims 1 to 9 lack novelty and inventive step that "Reference 1 teaches a method for preparing electrolytic manganese dioxide, wherein electrolysis is carried out with a solution of manganese sulphate and sulfuric acid as the electrolytic solution, and, in a method for preparing electrolytic manganese dioxide, electrolysis is carried out at an electrolysis temperature of 90°C, an

electrolysis current density of 40 A/m^2 , and a sulfuric acid concentration of 80 g/l ; it also teaches that the obtained specific surface area of the electrolytic manganese dioxide is $47 \text{ m}^2/\text{g}$; in addition, it teaches that the obtained electrolytic manganese dioxide can be used in manganese dry cell, in particular, alkaline manganese dry cell."

(2) However, taking a general look at the electrolysis conditions indicated in Comparative Example 1 of Reference 1, the manganese sulphate concentration is too low for preparing electrolytic manganese dioxide. In reality, electrolysis carried out with those electrolysis conditions resulted in the electrolysis voltage reaching 5 V at electrolysis day number 2, whereafter electrolysis became impossible, as indicated in the appended Experimental Results Certificate (1).

In order to obtain electrolytic manganese dioxide with the electrolysis conditions indicated in Comparative Example 1 of Reference 1, a special device or a special method not indicated in the contents of Reference 1 must be carried out; with a general method, preparing even electrolytic manganese dioxide is difficult. Further, that obtaining electrolytic manganese dioxide as recited in Claim 1 of the present application is much more difficult left aside, it is hardly believable that the content of Reference 1 describes the electrolytic manganese dioxide and positive electrode active material for battery using the same of Claim 1 of the present application.

(3) In addition, no description exists in Reference 1 that focuses on the weight loss at 200°C to 400°C or the content in bound waters that are lost by the step of heating at 200°C to 400°C , and since the electrolysis conditions indicated by the Examiner are electrolysis conditions of the Comparative Example of the invention of Reference 1, it does not constitute a motivation to test around these electrolysis conditions. Since this prior art is rather recognized as guiding in a direction that departs from the invention of the present case (refer to Guideline IV-8.8 (D)), the electrolytic manganese

dioxide and positive electrode active material for battery using the same of Claims 1 to 9 cannot be obvious for those skilled in the art to attain based on the content of the description of Reference 1.

(4) Please note that, in case the Examiner cannot be convinced, even with the above-mentioned explanations, the Applicant is prepared to bring corrections to the effect of removing entirely from Claim 1 the electrolytic manganese dioxide obtained by the electrolysis conditions indicated in Comparative Example 1 of Reference 1; please take this point in consideration as well.

2) Reply to opinion in regard to Reference 2

(1) The Examiner pointed out as reasons for Claims 1 to 9 lack inventive step that "in regard to electrolytic manganese dioxide used in manganese dry cell, Reference 2 teaches that when the bound water content rate is less than 3.0 wt%, the early discharge characteristics decrease. Inventing positive electrode active materials consisting of electrolytic manganese dioxide having not less than 3.0 wt% bound water content rate and battery using the same is easy for those skilled in the art from the suggestion in Reference 2 of the effect that the characteristics of the battery decrease when the bound water content rate is less than 3.0 wt%".

(2) However, determining the content in bound waters that are lost in the process of heating at 200°C to 400°C, as in the invention of the present case, and determining the content in bound waters that are lost in the process of heating at 120°C to 400°C, as in Reference 2, differ in technical meanings.

In Experimental Results Certificate (2), Sample A was prepared based on Comparative Example 1A of the present application, Sample B was prepared based on Example 9A of the present application, and Sample C was prepared based on Example 3A of the present application.

Here, what must be noticed are the points that when Samples A and B are compared, regarding the amount of weight lost at 120°C to 400°C, it is less for Sample B compared to Sample A, whereas regarding the amount of weight lost at 200°C to 400°C, it is the opposite, i.e., it is more for Sample B compared to Sample A. This fact means that, even if the content of bound waters that are lost in the process of heating at 120°C to 400°C is large, it does not necessarily follow that the content of bound waters that are lost in the process of heating at 200°C to 400°C is also large, demonstrating that the technical meanings are different.

In addition, when the battery characteristics (high rate pulse characteristics) of Samples A and B are compared, the results show that Sample B, which has a higher content in bound waters that are lost in the process of heating at 200°C to 400°C, demonstrates better battery characteristics (high rate pulse characteristics); this result can absolutely not be predicted by focusing on the content in bound waters that are lost in the process of heating at 120°C to 400°C.

As shown in the foregoing, determining the content in bound waters that are lost in the process of heating at 200°C to 400°C, as in the invention of the present case, and determining the content in bound waters that are lost in the process of heating at 120°C to 400°C, as in Reference 2, differ in technical meanings; furthermore, an effect that cannot be predicted by the invention of Reference 2 can be obtained by focusing on the content in bound waters lost in the process of heating at 200°C to 400°C to select the electrolytic manganese dioxide.

(3) Moreover, since there is not a single description focusing on the weight loss at 200°C to 400°C or the quantity of bound waters that are lost in the process of heating at this temperature range in the content of Reference 2, the electrolytic manganese dioxide of Claim 1, whose technical meaning is

different, cannot be obvious for those skilled in the art to devise based on Reference 2.

3) Reply to opinion in regard to Reference 3

(1) The Examiner pointed out as reasons for Claims 1 to 9 lack inventive step that "Reference 3 teaches that electrolytic manganese dioxide, whose number of moles of water eliminated by heat treatment in a range of not less than 120°C and not exceeding 400°C is not less than 0.16 per mole of Mn atom, serves as positive electrode active material of an aqueous solution system manganese battery. Then, waters of not less than 0.16 per mole of Mn atom are equivalent to not less than 3.2% based on calculation."

(2) However, as mentioned above, determining the content in bound waters that are lost in the process of heating at 200°C to 400°C, as in the invention of the present case, and determining the content in bound waters that are lost in the process of heating at 120 to 400°C, as in Reference 2, differ in technical meanings, such that even if the content of bound waters that are lost in the process of heating at 200°C to 400°C is large, it does not necessarily lead to the fact that the content of bound waters that are lost in the process of heating at 120°C to 400°C is also large.

(3) Moreover, since there is not a single description focusing on the weight loss at 200°C to 400°C or the quantity of bound waters that are lost in the process of heating at this temperature range in the content of Reference 3, the electrolytic manganese dioxide of Claim 1, whose technical meaning is different, and the positive electrode active material for battery consisting thereof cannot be obvious for those skilled in the art to devise based on Reference 3.

4) Reply to opinion in regard to Claims 2 to 9

Since Claims 2 to 9 are Claims that are dependent on Claim 1, as long as Claim 1 constitutes an inventive step, they obviously constitute an inventive step (refer to Guideline IV-8.10).

Note that in Claim 5, by rectifying what initially was "in a method ... to prepare electrolytic manganese dioxide" into "in the method ... to prepare electrolytic manganese dioxide as recited in Claim 1," Claims 5 to 8 became Claims that are dependent on Claim 1; please take notice.

6. List of Attachments

- 1) Experiment Certificate (1)
- 2) Experiment Certificate (2)

Amendment
(Amendment Under Article 11)

[seal: PCT, Received 10 June 2004]

To: Chikako Aoki, Patent Office Examiner

1. International Application: PCT/JP03/02640

2. Applicant

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4. Subject of Amendment

Claims

5. Content of the Amendment

(1) On page 19, Claims, Claim 5, add "as recited in Claim 1" behind "method
... to prepare electrolytic manganese dioxide."

List of Attachments

(1) Page 19, Claims

What is claimed is

1. A positive electrode active material for battery, wherein,
in a positive electrode active material for battery comprising of
electrolytic manganese dioxide,
said electrolytic manganese dioxide has a weight loss at 200°C to
400°C when said electrolytic manganese dioxide is heated of not less than
2.7 wt%.
2. The positive electrode active material for battery as recited in Claim 1,
wherein the specific surface area of said electrolytic manganese dioxide is
not more than 75 m²/g.
3. The positive electrode active material for battery as recited in Claim 1 or 2,
wherein the electric potential of said electrolytic manganese dioxide is 270
mV to 320 mV.
4. The positive electrode active material for battery as recited in any of Claim
1 to 3, wherein said electrolytic manganese dioxide is obtained by
electrolysis with a solution of manganese sulphate and sulfuric acid as the
electrolytic solution, at an electrolysis temperature of 85°C to 95°C, an
electrolysis current density of 20 A/m² to 50 A/m², and a sulfuric acid
concentration of 50 g/l to 100 g/l.
5. (after amendment) A method for preparing electrolytic manganese dioxide,
wherein, in a method wherein electrolysis is carried out with a solution of
manganese sulphate and sulfuric acid as the electrolytic solution to prepare
electrolytic manganese dioxide as recited in Claim 1,
electrolysis is carried out at an electrolysis temperature of 85°C to
95°C, an electrolysis current density of 20 A/m² to 50 A/m², and a sulfuric
acid concentration of 50 g/l to 100 g/l.
6. The method for preparing electrolytic manganese dioxide as recited in

Claim 5, wherein the obtained electrolytic manganese dioxide has a weight loss at 200°C to 400°C when said electrolytic manganese dioxide is heated of not less than 2.7 wt%.

7. The method for preparing electrolytic manganese dioxide as recited in Claim 5 or 6, wherein the specific surface area of the obtained electrolytic manganese dioxide is not more than 75 m²/g.

8. The method for preparing electrolytic manganese dioxide as recited in any of Claims 5 to 7, wherein the electric potential of the obtained electrolytic manganese dioxide is 270 mV to 320 mV.

June 4, 2004

Experimental Results Certificate (1)

(Created by)

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(Administrator)

Akira Oyama, Technology Deputy General Manager [seal: Oyama]
Battery Materials Division, Mitsui Kinzoku

1. Experiment Days

May 16th, 2004, to May 28th, 2004

2. Experiment Location

Technology Division, Battery Materials Division, Mitsui Kinzoku
Denman Electrolysis Test Room

3. Experimenters

Battery Materials Division, Mitsui Kinzoku
Takehara Battery Materials Plant
Name: Shinya Kagei [seal: Kagei]
Name: Yasuhiro Ochi [seal: Ochi]

4. Objective of the Experiment

To comparatively examine the preparation conditions of the
electrolytic manganese dioxide of Comparative Example 1 described in
Reference 1 (JP 2002-289185), which was cited in the first PCT opinion in

regard to the PCT Application (JP03/02640, hereinafter referred to as "the present application"), and the preparation conditions of the electrolytic manganese dioxide described in Example 1 of the present application.

5. Contents of the Experiment

1) Electrolysis was carried out based on the electrolysis conditions described in Comparative Example 1 of Reference 1.

With a 5-l beaker fitted with a heating device as the electrolytic bath, titanium plates as anodes and graphite plates as cathodes were each hung alternately, and a tube was provided at the bottom of the electrolytic bath for introducing an electrolysis supply solution consisting of manganese sulphate. Electrolysis was carried out while injecting the electrolysis supply solution into the electrolytic bath to adjust the composition of the electrolytic solution during electrolysis so as to obtain 20 g/l manganese and a sulfuric acid concentration of 80 g/l, and maintaining the temperature of the electrolysis bath at 90°C, at a current density of 40 A/m².

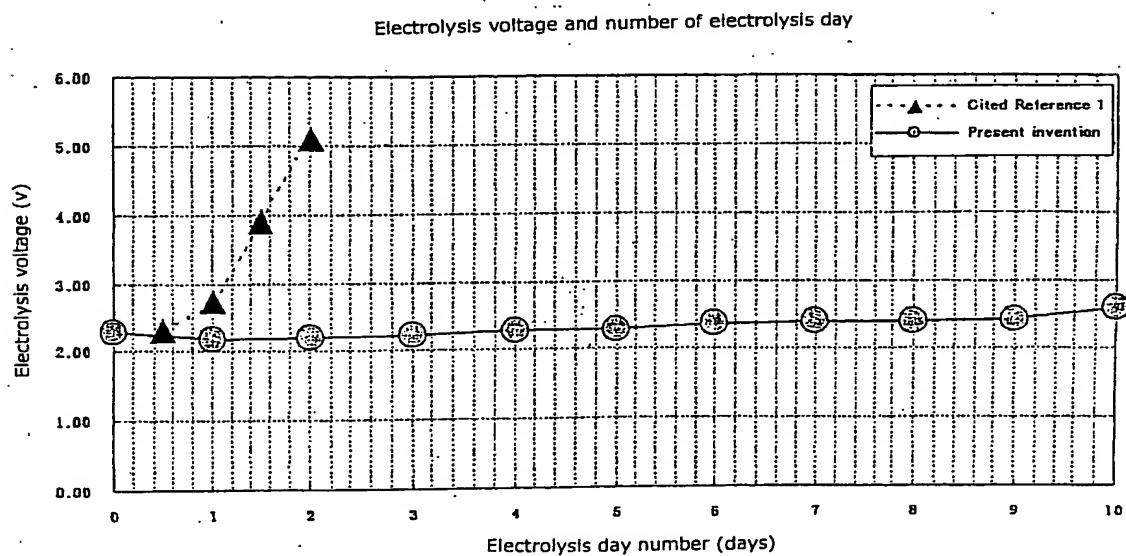
2) Electrolysis was carried out based on the electrolysis conditions described in Example 1 of the present application.

A 5-l beaker fitted with a heating device as the electrolytic bath, titanium plates as anodes and graphite plates as cathodes were respectively hung alternately, and a tube was provided at the bottom of the electrolytic bath for introducing an electrolysis supply solution consisting of manganese sulphate. Electrolysis was carried out while injecting this electrolysis supply solution to the electrolytic bath to adjust the composition of the electrolytic solution during electrolysis so as to obtain 40 g/l manganese and a sulfuric acid concentration of 75 g/l, and maintaining the temperature of the electrolysis bath at 90°C, at a current density of 35 A/m² for 10 days.

6. Experimental Results

As shown in the following figure, with the electrolysis conditions described in Reference 1 (Comparative Example 1), at number of electrolysis day=2, 5 V was reached, i.e., about three times the normal electrolysis voltage at the same period, and electrolysis became impossible. From this, it was revealed that with the electrolysis conditions indicated in Comparative Example 1 of Reference 1, electrolytic manganese dioxide cannot be obtained. The exact reason for such an outcome is undetermined; however, from technical common sense, it is believed that the manganese sulphate concentration was too small, and the electrolysis voltage increased due to the diffusion of manganese ions and the effect of oxidation. In any case, in order to obtain electrolytic manganese dioxide under the electrolysis conditions indicated in Comparative Example 1 of Reference 1, a special device or a special condition that is not indicated in Reference 1 is necessary.

(Experimental data)



End

June 4, 2004

Experimental Results Certificate (2)

(Created by)

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(Administrator)

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1. Experiment Days

April 19th, 2004, to May 28th, 2004

2. Experiment Location

Technology Division, Battery Materials Division, Mitsui Kinzoku
Electrolysis Test Room, Physical Test Room, Battery Performance Test
Room

3. Experimenters

Battery Materials Division, Mitsui Kinzoku
Battery Materials Plant
Name: Shinya Kagei [seal: Kagei]
Name: Yasuhiro Ochi [seal: Ochi]

4. Objective of the Experiment

To clarify the difference in technical meaning between the bound water content rate described in Reference 2 (JP9-188519), which was cited in the first PCT opinion in regard to the PCT Application (JP03/02640, hereinafter referred to as "the present application"), and the bound water content rate specified by the present invention.

5. Contents of the Experiment

<Differential thermal analysis conditions>

The weight loss at a given temperature range was measured using ThermoGravimetry/Differential Thermal Analyser: TG-DTA (Mac-Science TG-DTA2000S), under conditions of a sample amount of 40 mg, a sample container made of alumina, a temperature increase speed of 5°C/minute (normal temperature to near 560°C), a sampling time of one second, air as the ambient gas (100 ml/minute), alumina powder as the reference substance, and a device ambient temperature of 15°C to 30°C.

<Sample preparation method>

(Sample A: based on Comparative Example 1A of the present application) With a 5-l beaker fitted with a heating device as the electrolytic bath, titanium plates as anodes and graphite plates as cathodes were each hung alternately, and a tube was provided at the bottom of the electrolytic bath for introducing an electrolysis supply solution consisting of manganese sulphate. Electrolysis was carried out while injecting the electrolysis supply solution into the electrolytic bath to adjust the composition of the electrolytic solution during electrolysis so as to obtain 40 g/l manganese and a sulfuric acid concentration of 75 g/l, and maintaining the temperature of the electrolysis bath at 90°C, at a current density of 55 A/m² for 20 days.

(Sample B: based on Example 9A of the present application)

With a 5-l beaker fitted with a heating device as the electrolytic bath, titanium plates as anodes and graphite plates as cathodes were each hung alternately, and a tube was provided at the bottom of the electrolytic bath for introducing an electrolysis supply solution consisting of manganese sulphate. Electrolysis was carried out while injecting the electrolysis supply solution into the electrolytic bath to adjust the composition of the electrolytic solution during electrolysis so as to obtain 40 g/l manganese and a sulfuric acid concentration of 75 g/l, and maintaining the temperature of the electrolysis bath at 98°C, at a current density of 35 A/m² for 20 days.

(Sample C: based on Example 4A of the present application)

With a 5-l beaker fitted with a heating device as the electrolytic bath, titanium plates as anodes and graphite plates as cathodes were each hung alternately, and a tube was provided at the bottom of the electrolytic bath for introducing an electrolysis supply solution consisting of manganese sulphate. Electrolysis was carried out while injecting the electrolysis supply solution into the electrolytic bath to adjust the composition of the electrolytic solution during electrolysis so as to obtain 40 g/l manganese and a sulfuric acid concentration of 75 g/l, and maintaining the temperature of the electrolysis bath at 90°C, at a current density of 20 A/m² for 20 days.

<LR6 battery preparation conditions>

LR6 (size AA) type alkaline manganese batteries were made with electrolytic manganese dioxide as positive electrode active materials. Here, an aqueous solution of potassium hydroxide at a concentration of 40% saturated with zinc oxide, to which on the order of 1.0% carbomethoxy cellulose and sodium polyacrylate were added as gelling agents, was used as the electrolytic solution of the battery. In addition, 3.0 g of zinc powder was used as negative electrode active material; this negative electrode active material

and 1.5 g of the above-mentioned electrolytic solution were mixed and gelled and directly used as a negative electrode material. A longitudinal cross-sectional view of an alkaline manganese battery made in this way is shown in Fig. 1.

As shown in Fig. 1, the alkaline manganese battery pertaining to the present invention is provided with a positive electrode active material 2 consisting of electrolytic manganese dioxide positioned inside a positive electrode can 1, and a negative electrode material 4 consisting of gelled zinc powder positioned on the inside of the positive electrode active material 2 via a separator 3. A negative electrode collector 5 is inserted inside the negative electrode material 4; this negative electrode collector 5 passes through a seal 6 that plugs the lower portion of the positive electrode can 1 and is joined to a negative electrode bottom plate 7 provided below the seal 6. On the other hand, a cap 8 that is to be the positive terminal is provided on the top side of the positive electrode can 1. Insulation rings 9 and 10 that vertically sandwich the cap 8 and the negative electrode bottom plate 7 are provided; a heat shrink resin tube 11 and an external cover can 12 that covers the tube 11 are provided to cover the circumference of the positive electrode can 1 while stabilizing the cap 8 and the negative electrode bottom plate 7 via these insulation rings 9 and 10.

[Fig. 1] Cross-sectional view of alkaline manganese battery

<Battery characteristics measurement conditions>

With the alkaline manganese battery, 10 seconds ON, 50 seconds OFF pulse-repeated discharging was performed with a discharge current of 1500 mA at 20°C, and the number of pulses until the cut voltage (stop voltage) of

0.9 V was measured. The pulse characteristics were evaluated with the values of Comparative Example 1A as 100%.

6. Experimental Results

Sample species	Quoted Reference conditions	Measurement conditions of the present application		Battery performance
		120°C - 400°C	200°C - 400°C	
Sample A	3.70%	2.68%	100	
Sample B	3.67%	3.01%	105	
Sample C	4.06%	3.12%	112	